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THE USE OF ACRYLATES IN ALUMINUM TANNING*

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ABSTRACT

The quality of aluminum-tanned leather can be greatly improved by the use of polyacrylates to fix the aluminum more firmly in the leather.

INTRODUCTION

Aluminum is one of the most abundant elements, and its salts are cheap and easily available. They have been used for centuries for the tannage of light skins to make a white, flexible leather of good color, feel, and appearance.

In spite of its advantages aluminum has never played a major role in the production of leather, and for many uses alum-tanned leathers‡ have been almost entirely replaced by leathers tanned with chromium salts. Although chromium salts are more expensive than aluminum salts and give a leather with a bluish or greenish cast, they have the advantage of producing a stable combination with hide. When alum leather made by usual tanning methods is washed, the water removes most of the loosely combined alum, leaving the leather in a hard, horny condition.

Several new developments suggest that the reevaluation of alum tannage might be advantageous. One of these is the growing demand in metallurgy for chromium ores, which are relatively scarce. In 1953, 1,118,400 tons of chromite of 42.7% Cr_2O_3 were used in steelmaking in the United States. In the same year this country produced only 33,000 tons of ore containing 47% Cr_2O_3, in Oregon, and about 100,000 tons of 35% ore in Montana. Even with full production from these sources, and adding the low-grade ore that may be obtained from Cuba, the total production would be only 10 to 15% of what is required for metallurgy in this country. The nearest large source of chromium ores is in South Africa, and shipping from such a distant point is not only expensive but uncertain in time of war (1). It would appear to be advantageous for tanners to have an alternate tanning method in case a shortage of chromium develops.

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‡The term "Alum-tanned leather", as used in this paper, means a leather tanned with any salt of aluminum, not necessarily the double sulfate commonly known as alum.

Interest in alum tannage has also been stimulated by the increase in our knowledge of the mechanism of tannage (2,3). Previously the stability of alum-tanned leather was not good, because in practice liquors could not be made basic enough for proper tannage without precipitation of the aluminum. It has now been found that the addition of salts of organic hydroxyacids to alum liquors produces a "masking" action, permitting the basicity of the liquors to be raised considerably without precipitation of the aluminum. A similar effect is obtained by using the aluminum salt of the organic acid. However, there is a limit to the amount of masking salt which may be used. The combining power of the aluminum with the collagen is weakened by the presence of these materials, and at high concentrations of masking salts it may be completely lost. At low concentrations this effect is counterbalanced by the increased basicity of the liquor brought about by their use and also by a more uniform distribution of the alum through the hide. However, a higher degree of combination between aluminum and collagen is desired than can be obtained by use of masking salts.

Many types of materials, such as synthetic resins, have been proposed for tanning purposes. If such a material would also combine with aluminum and with the skin, a more thoroughly fixed tannage could be effected. Several materials have been tested for this purpose. Experiments with polyacrylates are described in this paper. Polyacrylates are readily formed by the polymerization of acrylic acid ($CH_2=CH\ CO_2H$) or its salts. These compounds are known to form complexes with copper, magnesium, calcium, etc. (4,5,6). Acrylates have been proposed as tanning agents (7), either alone or as a combination tannage with other materials, including alum. However, in the present tests the function of the polyacrylate was not primarily to give a tannage but rather to hold the aluminum oxide more firmly.

Preliminary tests showed that when polyacrylates and alum tannages were applied simultaneously, a poor grain was obtained on the leather. When applied consecutively in either order, however, the two treatments were compatible. This tannage involves the interaction of such factors as the degree of polymerization of the acrylate, the type of acrylate salt (sodium, potassium, ammonium, etc.), the ratio of acrylate to aluminum salt, the pretreatment of the hide or skin, and the concentration and pH of the solutions. The data presented in this paper show typical results obtained by the variation of some of these factors.

EXPERIMENTAL

Solutions.—The solutions were made to approximately pH 4.5 because the optimum pH for fixation of aluminum is between 4.2 and 4.8. A basic aluminum acetate solution was used for tannage rather than a masked sulfate or chloride liquor because of ease of operation. Tests have been made with polyacrylic acid and several of its salts. The tests reported here were made with the sodium salt of low-molecular weight polymers (mol. wt. 20 to 30 thousand).

Tannage.—Commercial pickled calfskins were cut into 4″ x 6″ pieces. The pieces used in each series were cut from the same area of the skin. The pieces were shaken in mason jars with the aluminum compound or polyacrylate solution at 20 rpm for 10 min. every hour, then allowed to stand overnight when required. The float ratio used was 5 to 1. After each treatment, and at the completion of tannage, the skins were washed for 5 to 10 min. They were fatliquored with a nonionic-type oil and plated out to dry at room temperature. All concentrations (percentages) of aluminum salt and acrylate used were based on the drained weights of the skins.

The following experiments were performed to determine the influence of concentration of reagents, the order of application, and duration of treatment on the effect of polyacrylates on the fixation of alum. Results of studies where the amount of polyacrylate was varied from 0.5 to 2.5% while the aluminum compound was kept constant (3.0% Al_2O_3) are presented in Table I. Each reagent was applied for 24 hr.; in one series the calfskin pieces were treated first with aluminum acetate followed by acrylate, and in another series the acrylate was applied first. Results of studies where the amount of aluminum salt was varied from 1.0 to 5.0% Al_2O_3 while the acrylate was kept constant (2.0%) are presented in Table II. The calfskin pieces were treated for 24 hr. with each reagent; in one series the aluminum acetate was applied before the acrylate, while in the other series the order was reversed. To determine the effect of duration of treatment, calfskin pieces were treated with aluminum salt (3.0% Al_2O_3) for 16 hr., followed by acrylate (2.0%) for periods varying from 4 to 24 hr. In a second series the calfskins were first treated with aluminum salt (3.0%) for periods varying from 2 to 24 hr. and followed by polyacrylate (2.0%) for 7 hr. The results are presented in Table III.

Evaluation of leather.—The following tests and determinations were made on the finished leather:

Stitch Tear. Stitch tear was determined by the methods of the American Leather Chemists Association (8). A single measurement was made on each leather piece.

Combined Al_2O_3. To determine the combined Al_2O_3, 3 grams of leather were extracted with 500 ml. of water at 35°C. for 3 hr. The ash and Al_2O_3 in the original leather and in the wash water were determined by the usual analytical methods. The difference between the total Al_2O_3 and the Al_2O_3 in the wash water represents the combined or fixed Al_2O_3. The values were checked periodically by determining the Al_2O_3 in the extracted leather.

DISCUSSION

Table I shows that when pickled calfskins were first tanned with alum, the amount of acrylate used did not affect appreciably the quantity of alum fixed,

TABLE I

TANNAGE OF PICKLED CALFSKIN PIECES WITH ALUMINUM ACETATE AND VARYING AMOUNTS OF ACRYLATE

Acrylate Used* %	Final pH of Liquor		Properties of Leather Produced			
	Alum†	Acrylate	Fixed Al_2O_3 %	Shrinkage Temp. °C.	Stitch Tear‡ lbs/in	Remarks
Aluminum salt applied first						
0.5	4.5	4.9	2.0	89	722	All pieces have good color and appearance with a smooth grain. First piece moderately flexible; succeeding pieces increasingly stiffer.
1.0	4.5	4.9	1.9	81	750	
1.5	4.5	4.9	1.9	82	716	
2.0	4.5	5.0	2.1	86	883	
2.5	4.5	5.9	1.9	81	827	
Acrylate applied first						
0.0	4.7	—	1.8	80	—	All pieces have good color and appearance with a smooth grain. All pieces more flexible than first group. Stiffness increases with increasing amount of acrylate.
0.5	4.6	2.7	1.8	84	997	
1.0	4.6	3.3	2.2	80	1100	
1.5	4.6	3.7	2.3	78	1025	
2.0	4.6	4.1	2.6	81	1053	
2.5	4.7	4.5	2.6	84	1198	

*Based on drained weight of skin.
†A basic aluminum acetate solution was used containing 3% Al_2O_3 based on drained weight of the skins used. Time of each treatment was 24 hr.
‡Stitch tears are comparable for any table, but are not comparable between tables as samples for the different series were taken from different portions of skin.

the shrinkage temperature, or the stitch tear strength. However, when the acrylate was applied first, the aluminum fixation was raised by an increase in the amount of acrylate used, reaching a maximum when 2% acrylate was used. At this point the aluminum fixation was about 44% greater than that in the control piece with no acrylate. The stitch tear increased slightly with increase in the concentration of acrylate used. There was an increase in the stiffness of the leather with increased concentration of acrylate; this was more pronounced when the alum was applied first. The increase was slight; mechanical measurements of flexibility and compressibility showed no significant differences in the properties of the tanned specimens.

Data in Table II indicate that there was progressively greater fixation of aluminum with increasing concentration of aluminum in the tanning solution. Furthermore, with the exception of the 5.0% levels the amount of aluminum fixed was increased by pretannage with acrylate. At present we have no explanation for the apparent anomaly at the 5.0% level. When the

TABLE II

ALUM TANNAGE OF PICKLED CALFSKIN PIECES BY VARYING THE AMOUNT OF Al_2O_3 AND KEEPING THE AMOUNT OF ACRYLATE CONSTANT

Al_2O_3† %	Final pH of Liquor		Properties of Leather Produced			
	Alum	Acrylate*	Fixed Al_2O_3 %	Shrinkage Temp. °C.	Stitch Tear‡ lbs/in	Remarks
Alum applied first						
1.0	4.0	5.1	0.8	67	1176	Pieces had good color and fair grain. Leather became plumper and more flexible with increasing amounts of alum.
2.0	4.2	5.1	1.7	78	986	
3.0	4.3	5.1	2.2	85	778	
4.0	4.4	5.1	2.2	86	866	
5.0	4.5	5.1	3.5	88	1030	
Acrylate applied first						
1.0	4.5	4.1	1.4	71	1366	Good color and grain. Low concentrations slightly plump and quite flexible. Plumpness and stiffness increase with concentration.
2.0	4.6	4.1	2.5	73	1215	
3.0	4.7	4.1	2.6	81	1137	
4.0	4.7	4.1	2.7	83	1053	
5.0	4.7	4.1	3.2	83	935	

*2% acrylate based on the drained weight of the skins used. Time of each treatment was 24 hr.
†A basic aluminum acetate solution was used containing the required amount of Al_2O_3 based on the drained weight of the skins.
‡Stitch tears are comparable for any table but are not comparable between tables.

aluminum was applied first, the leather showed greater flexibility as the concentration of aluminum salt used was increased. When acrylate was used first, the leather became stiffer with increased amounts of Al_2O_3. Again this increase in stiffness was not significant.

TABLE III

EFFECT OF TIME ON THE ALUM-ACRYLATE TANNAGE OF PICKLED CALFSKIN PIECES*

Hr. of Tannage		Final pH of Liquor		Properties of Leather Produced			
Alum	Acrylate	Alum	Acrylate	Fixed Al_2O_3 %	Shrinkage Temp. °C.	Stitch Tear† lbs/in	Remarks
16	4	4.5	5.4	1.4	82	1512	Rather stiff
16	7	4.4	5.5	1.7	88	1394	Stiff but flexible
16	16	4.6	5.5	2.0	89	1579	Flexible
16	24	4.5	5.6	2.2	89	1512	Flexible
2	7	4.6	5.5	1.4	86	1534	Stiff and tinny
4	7	4.4	5.5	1.6	86	1568	Better than preceding, slightly stiff and tinny
7	7	4.4	5.5	1.6	89	1445	Flexible
16	7	4.4	5.5	1.7	88	1366	Flexible
24	7	4.3	5.5	2.0	89	1204	Flexible

*The treatment was with a basic aluminum acetate solution containing 3% Al_2O_3, followed by a treatment with 2% acrylate, each based on the drained weight of the skin.
†Stitch tears are comparable for any table, but are not comparable between tables.

Table III shows that for each treatment an increase of time beyond 7 hr. increases the amount of fixed Al_2O_3 but apparently does not improve the quality of the leather as judged by appearance and feel.

SUMMARY

The fixation of Al_2O_3 in alum leather can be greatly increased by treatment with acrylates. The leather produced is white, flexible, full, and of high strength as measured by stitch tear resistance. Better fixation is obtained if acrylates are applied first, followed by alum, than if the reverse order is followed. The leather might replace chrome leather for many purposes for which a white leather is desired.

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DISCUSSION

CARL G. TELANDER (Raser Tanning Co.): At one time there was a considerable interest in alum tannage, and a good deal of work was performed with quite encouraging results. But somehow the subject became controversial, and there were two schools of thought on the serviceability of the leather. I am now speaking generally of alum retannage of vegetable-tanned leather, but the reopening of the question in any type of tannage and leather is still appreciated. Earlier results on alum tannage and alum retannage were quite encouraging, and if the same effort were put into further development as has been put into many other types of tanning developments, an interest could be built up in the trade, which could only result in quality improvement and a better position for leather in general.